

# Thermal Expansion and Diffusion Coefficients of Carbon Nanotube-Polymer Composites

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## ABSTRACT

Classical molecular dynamics (MD) simulations employing Brenner potential for intra-nanotube interactions and van der Waals forces for polymer-nanotube interface are used to investigate the thermal expansion and diffusion characteristics of carbon nanotube–polyethylene composites. Additions of carbon nanotubes to a polymer matrix are found to increase the glass transition temperature  $T_g$ , and thermal expansion and diffusion coefficients in the composite above  $T_g$ . These findings could have implications in CNT composite processing, coating and painting applications.

Carbon nanotubes (CNTs) are nanoscaled materials that are found to have unusual mechanical and electronic properties.<sup>1</sup> The strong in-plane graphitic C–C bonds make them exceptionally strong and stiff against axial strains and very flexible against nonaxial strains. Additionally, CNTs can be metallic or semiconducting, determined by their atomic configurations such as chirality and diameter. Many applications of CNTs, such as in nanoscale molecular electronics, sensing and actuating devices or as reinforcing additive fibers in functional composite materials, have been proposed. Several recent experiments on the preparation and mechanical characterization of CNT-polymer composites have also appeared.<sup>2–4</sup> These measurements suggest modest enhancements in strength characteristics of CNT-embedded matrixes as compared to bare polymer matrixes.<sup>4</sup> Preliminary experiments and simulation studies on the thermal properties of carbon nanotubes show very high thermal conductivity.<sup>5</sup> It is expected, therefore, that nanotube reinforcements in polymeric materials may also significantly change the thermal and thermo-mechanical properties of the composites.

Using classical molecular dynamics (MD) simulations (DLPOLY MD program<sup>6</sup>), we investigate the thermo-structural behavior of CNT reinforced polyethylene (PE) composites. The structural and diffusion characteristics of the composite have been studied in the temperature range below and above glass transition temperature  $T_g$ . We report significant enhancements of thermal expansion and diffusion coefficients of the composite above  $T_g$ .

The interactions of the carbon atoms within nanotubes are described by Tersoff–Brenner many-body potential,<sup>7,8</sup> which is fitted to describe carbon and hydrocarbon systems. This potential has been used to study the elastic properties of carbon nanotubes and gives results comparable to those from Tight Binding or Density Functional Theory (DFT) based methods. The nanotube–polymer interface is described via nonbonding van der Waals interactions (VDW) of truncated Lennard–Jones (LJ) 6–12 type with  $\epsilon = 0.461$  kJ/mol and  $\sigma = 3.65$  Å. A united-atom model is used to describe individual polymer chains, in which each CH<sub>2</sub> or CH<sub>3</sub> group is considered as a single interaction unit. This model is commonly used to avoid high-frequency vibrations of the C–H bonds. Intra-polymer potential by Clarke et al.<sup>9</sup> has been used to describe interactions within a polymer chain.

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This potential has two components: valence angle potential and torsion potential. The valence angle potential is described as

$$\Phi(\theta) = 0.5k_{\theta}(\cos\theta - \cos\theta_0)^2$$

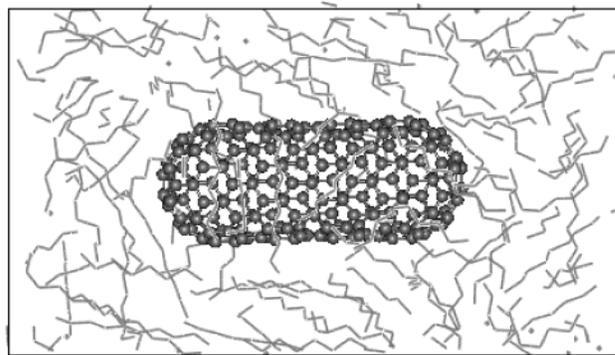
where  $k_{\theta} = 520 \text{ J} \cdot \text{mol}^{-1}$ ,  $\theta_0 = 112.813^\circ$ , and the torsion potential is described as

$$\Phi(\alpha)/\text{J} \cdot \text{mol}^{-1} = C_0 + C_1 \cos\alpha + C_2 \cos^2\alpha + C_3 \cos^3\alpha$$

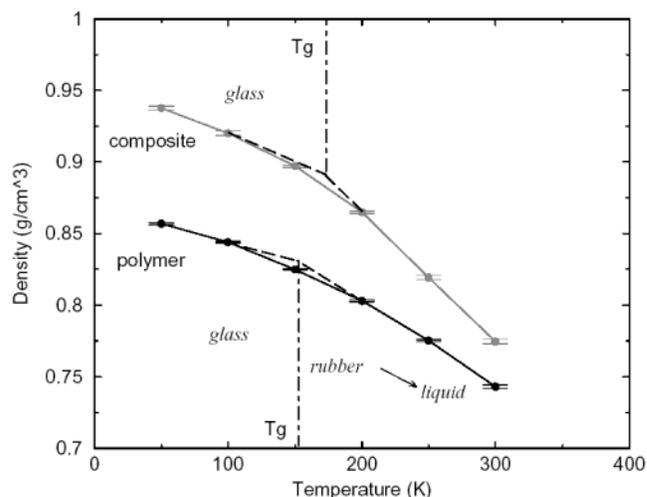
where  $C_0 = 8832$ ,  $C_1 = 18\,087$ ,  $C_2 = 4880$ , and  $C_3 = -31\,800$ . In general, the C–C bonds in a polymer chain are typically kept rigid to allow large MD time steps during the simulations. However, we have allowed full dynamics of these bonds, to be consistent with the dynamics of C–C bonds within CNTs. A harmonic potential  $0.5 k_b(l - l_0)^2$  is used for the dynamics of C–C bonds within a chain, where  $k_b = 346 \text{ KJ} \cdot \text{mol}^{-1}/\text{\AA}^2$  and  $l_0 = 1.53 \text{ \AA}$ .<sup>10</sup> Truncated 6–12 LJ potentials are applied to pairs of units that are apart by more than three units with  $\epsilon = 0.498 \text{ KJ} \cdot \text{mol}^{-1}$  and  $\sigma = 3.95 \text{ \AA}$ . The time-step of 0.5 fs is used in our MD simulations.

Conformations of long-chained polymer molecules are important in describing the dynamics and properties of bulk polymers.<sup>11</sup> Studies have shown that MD is very slow to relax a polymer chain to its equilibrium conformation. This difficulty can be avoided by using Monte Carlo (MC) simulations. The MC simulations were run for each chain at 300 K for up to two million steps, such that the end-to-end distances of polymer chains show the square-root dependence on chain lengths. This is in agreement with the prediction of Flory's theory.<sup>12</sup> The MC relaxed chains were then used in MD equilibrations of bulk configurations with periodic boundary condition, and the initial overlapping of chains was removed by gradually turning on the VDW interactions.

For composite systems, we have considered Single Wall CNTs (SWCNTs) as embedded fibers in this initial study because many reported experiments are based on SWCNTs dispersed or aggregated in polymer solutions.<sup>2,3,4</sup> The simulations of composites with Multiwalled CNTs (MWCNTs) will be considered and published in future. The small sized polymer and its CNT composite samples are considered first. For bulk PE, the samples consist of 80 short chains, with repeating units of  $N_p = 10$  in each chain (total 800 atoms in the unit cell). For CNT composite samples, the simulation cell additionally has a 20 Å long capped (10,0) CNT (total of 204 atoms) embedded in the polymer matrix with the volume fraction of about 8% of CNT in the cell. Periodic boundary condition is used and an illustration of the simulation cell is shown in Figure 1. The initial unit cell size is  $28 \times 28 \times 30 \text{ \AA}$  for both polymer and composite systems. The Evans NVT ensemble<sup>13</sup> MD was first run for 100 ps at  $T = 300 \text{ K}$ , followed by a 100ps run of Berendsen NPT ensemble<sup>14</sup> ( $P = 1 \text{ bar}$ ,  $T = 300 \text{ K}$ ) MD to help each sample reach their initial equilibrium configurations. The samples were then gradually cooled to 10 K at a rate of 1



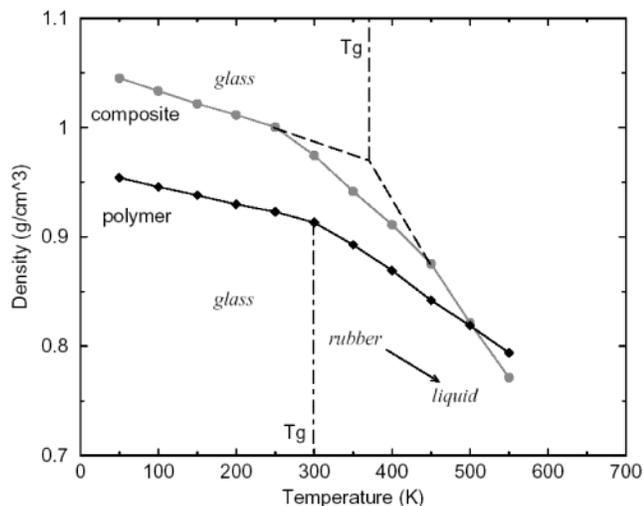
**Figure 1.** MD simulation unit cell for a composite system with 20 Å long capped (10,0) CNTs embedded in the polyethylene matrix. Periodic boundary condition is used.



**Figure 2.** Density as a function of temperature for short-chained PE ( $N_p=10$ ) and its composite with 20 Å long (10,0) CNTs embedded (averaged from 6 sample sets, the error bars are shown in the plot). Below  $T_g$ , the systems are in glassy state, and above  $T_g$ , the systems will be in rubber-like or liquid state, if temperature is higher than melting temperature  $T_m$ .

K/ps, and each system was further equilibrated for 100 ps at the chosen temperatures at which data were taken.

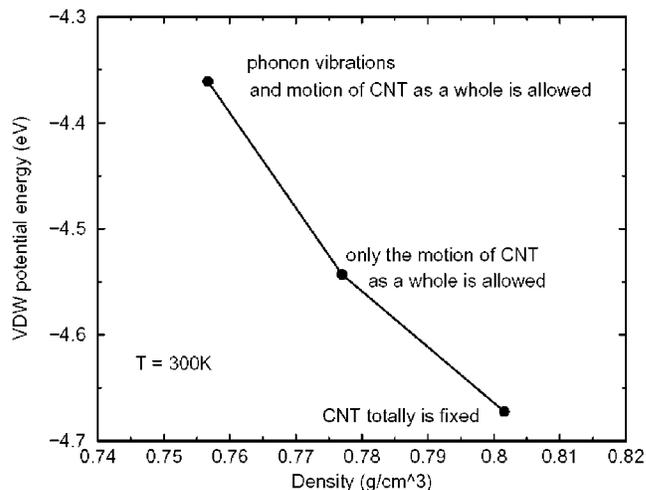
Figure 2 shows the densities of both the bulk PE and PE-CNT composites as a function of temperature. Each data point represents an average over the simulations of 6 sample sets with different initial conditions. The location of the discontinuity in the slope of the density vs temperature plot indicates the position of the glass transition temperature ( $T_g$ ). Experiments have reported  $T_g$  for bulk PE varying from 180 K to 250 K, depending on molecular weights and degrees of cross-linking in the samples.<sup>15</sup> Our computed  $T_g$  of about 150 K for pure PE samples is in agreement with previous MD simulations conducted on similar sized samples.<sup>10</sup> The nanotube-polymer composite, shown in Figure 2, has a higher  $T_g$  of 170 K, as the CNT in the matrix tends to slow the motions of the surrounding molecules below  $T_g$ . It is possible that the cross-linking of polymer matrix with embedded CNTs may further reduce the motions of polymer molecules and increase the  $T_g$ . Recent experiments on epoxy composite with 1% CNT indicate an increase of  $T_g$  about 10 °C.<sup>17</sup>



**Figure 3.** Density as a function of temperature for long-chained ( $N_p = 100$ ) PE and its composite with 200 Å long (10,0) CNTs embedded. Below  $T_g$ , the systems are in glassy state, and above  $T_g$ , the systems will be in rubber-like or liquid state, if temperature is higher than melting temperature  $T_m$ .

The decreasing densities of the bulk polymer and the composite with increasing temperatures indicate the thermal expansions of the materials. The slope of the curve at a given temperature gives the volume thermal expansion coefficient as  $(1/v) (\partial v/\partial T)$ . Figure 2 shows that above  $T_g$  (170 K), the volume thermal expansion increases more rapidly in the composite as compared to that in bulk PE. The volume thermal expansion coefficient of the composite is found to be  $4.5 \times 10^{-4} \text{ K}^{-1}$  below  $T_g$ , which is about 18% larger than  $3.8 \times 10^{-4} \text{ K}^{-1}$  of the bulk polymer in the same temperature range. Above  $T_g$ , the volume thermal expansion coefficient of the composite is found to be  $12 \times 10^{-4} \text{ K}^{-1}$ , and is increased as much as 40% compared to  $8.6 \times 10^{-4} \text{ K}^{-1}$  of the bulk PE within the same temperature range.

Our simulations on a larger system have verified this increase of thermal expansion coefficient of the CNT composites. For bulk PE, the sample consisted of 50 polymer chains, with repeating units of  $N_p = 100$  in each chain (for a total of 5000 united atoms). For CNT composites, a 200 Å long (10,0) CNT (with 1804 C atoms) is embedded in the PE matrix for each unit cell. The samples were prepared with the similar procedures described above. Figure 3 shows a similar increase of the thermal expansion in the composite at high temperatures. The volume thermal expansion coefficient of the composite is found to be  $16.1 \times 10^{-4} \text{ K}^{-1}$  ( $T > 400 \text{ K}$ ),  $6.9 \times 10^{-4} \text{ K}^{-1}$  ( $300 \text{ K} < T < 400 \text{ K}$ ), and  $2.2 \times 10^{-4} \text{ K}^{-1}$  ( $T < 300 \text{ K}$ ), respectively. For PE matrix, the expansion coefficient is  $6.6 \times 10^{-4} \text{ K}^{-1}$  ( $T > 300 \text{ K}$ ) and  $1.69 \times 10^{-4} \text{ K}^{-1}$  ( $T < 300 \text{ K}$ ), respectively. An increase of 142% in the thermal expansion coefficient of the composite at  $T > 400 \text{ K}$  is found. Experiments<sup>18</sup> have found that the volume expansion coefficient of bulk PE is around  $1.0 \times 10^{-4} \text{ K}^{-1}$  at room temperature. The MD simulations on smaller sized samples show a larger thermal expansion coefficient, whereas the expansion coefficient in the larger size samples is in better agreement with experimental data

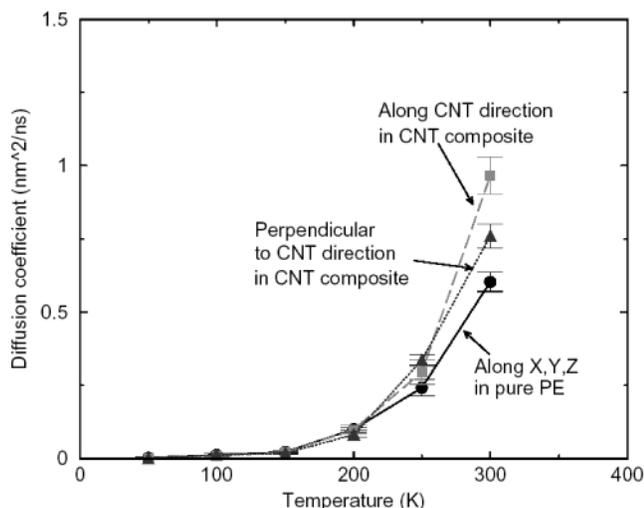


**Figure 4.** Change on density of the CNT composite with phonon modes and Brownian motions frozen for the smaller-sized system at  $T = 300 \text{ K}$ . Both thermal motions contribute to the excluded volume of embedded CNTs, which lead to the increased thermal expansion. The VDW energy of the system is increased with more allowed freedoms of motions of the embedded CNT.

(which are for heavily polymerized systems). The  $T_g$  for the larger sample size case is found to be around 300 K, which is higher than  $T_g$  for small sample cases discussed above. This is due to the dependence of the  $T_g$  on molecular weights of polymer chains. Previous MD simulations on long chained PE systems show  $T_g$  in the range of 230 K to 350 K,<sup>9,18</sup> which is similar to our computed  $T_g$  for the long chain systems.

The cases of using short PE chains with long embedded CNTs, or vice versa, are expected to give results different from the cases reported here, where both PE and CNTs are either short or long. This is because that the self-diffusion of chains along the sidewall of the CNT is dependent on the length ratio of the two systems. This will be investigated in detail and reported elsewhere.

The origin of higher thermal expansion coefficients in the composites is explained as follows. The CNT embedded within a polymer matrix has a fixed volume and excludes the occupancy of the polymer chains. The enhanced thermal expansions of the composites are attributed to the increase in the excluded volume of embedded CNTs as a function of temperature. To verify this concept, the MD simulations for the smaller-sized composite sample at 300 K were repeated under two constraints: (1) the phonon mode vibrations within a nanotube are frozen by increasing the stiffness of C–C bonds and by allowing only the motions of the CNT as a whole; (2) in addition to the first, the nanotube as a whole is frozen as well. Results under the second constraint, for a completely frozen CNT, show that the density of the composite reverts back. The density of the composite under the first constraint is intermediate between the completely frozen case and the completely free case. The energy from the VDW interactions is increased with more allowed motions of the CNT (as shown in Figure 4). These results suggest that both the phonon modes and Brownian motions of the CNT contribute to the excluded volume, and hence to the increase in thermal expansion coefficients.



**Figure 5.** Diffusion coefficient of polymer chains in pure PE matrix (short chained systems), and the CNT composite systems (both averaged from 6 sample sets). With the presence of CNTs, the diffusion coefficient is increased at high temperatures ( $T > T_g$ ) and the component parallel to CNT axis has a larger contribution compared with the perpendicular one.

Last, in Figure 5, we show the diffusion coefficients ( $\langle \Delta r^2 \rangle / \Delta t$ ) of the C atoms of the polymer matrix for the small-sized systems of the bulk PE and the composite cases. It is clear that in the composite case, the polymer chains are more diffusive at temperatures above  $T_g$ . Further more, the increase in the diffusion coefficient parallel to the CNT axis is about 30% larger than the increase perpendicular to the tube axis. This correlates well with the higher thermal expansion coefficient (above  $T_g$ ) data described above, and shows that the increased phonon vibrations and Brownian motions of the CNT are not only coupled efficiently to the motions of the polymer chains but also the coupling is anisotropic. This means that polymer chains parallel to the tube axis will flow or diffuse better at higher temperatures. Recent experiments on CNT-ABS and CNT-RTV composites, by Rick Berrera's group at Rice University, have shown large increases of diffusion coefficients in the matrixes.<sup>19</sup>

The importance of these findings has implications in the processing and applications of CNT reinforced polymer composite materials. The higher diffusion coefficient of the matrix atoms above  $T_g$  will allow increased mobility of composite materials during processing steps such as continuous spinning, weaving, and extrusion of the materials for fabrication purposes, and also possibly the smoother flow

through nozzles for painting or coating applications. The increased thermal expansion and diffusion coefficients, above  $T_g$ , may make it possible to significantly increase the thermal conductivity of CNT composites as well.

In summary, we have used MD simulations to study temperature dependent structural behavior of PE-CNT composites. The results show that the thermal expansion coefficient of the composite and diffusivity of polymer molecules increases significantly above glass transition temperature of the composite.

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